precipitated from solution, mp after recrystallization from acetone, 170–172°. It was identified by ir, mass spectrum, hydrolysis products, and comparison with the synthetic sample.

*Anal.* Calcd for $C_{32}H_{20}O_4$: C, 82.04; H, 4.30. Found: C, 81.85; H, 4.30.

Kinetics and Mechanism of the Sulfoxide–Silane Reaction
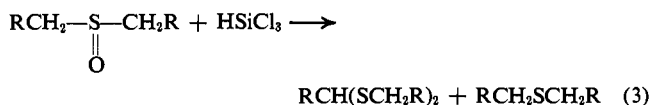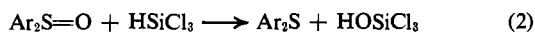
T. H. Chan and A. Melnyk

Contribution from the Department of Chemistry, McGill University, Montreal, Canada. Received November 22, 1969

Abstract: The kinetics of the reaction between aromatic sulfoxides and trichlorosilane have been examined. The reaction follows the rate equation, rate $= k$ [sulfoxide] [trichlorosilane]. The solvent and the substitution effect have been investigated. An isotope effect of $k_H/k_D = 2.0$–2.4 is observed. The activation parameters are $\Delta H^{\neq} = 7.1 \pm 0.5$ kcal/mol and $\Delta S^{\neq} = -31 \pm 1.4$ eu. Based on these observations, a mechanism involving a four-center transition state is proposed.

Because of the probable polarization of the Si–H bond into $Si^{\delta+}$–$H^{\delta-}$, silicon hydrides reduce a number of organic functional groups.[1] Their use as synthetic reagents has, however, been superseded by aluminum hydrides and borohydrides. Recently, Fritzche, *et al.*,[2] observed that silanes are superior to lithium aluminum hydride (LAH) in the reduction of phosphine oxides to phosphines even though LAH is a stronger reducing agent. The reason for this can be readily understood if one examines reaction 1. It is

$$R_3P{=}O + HSiCl_3 \longrightarrow R_3P + HOSiCl_3 \qquad (1)$$
$$\downarrow HSiCl_3$$
$$H_2 + Cl_3SiOSiCl_3$$
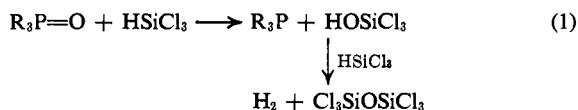
essentially an oxygen-transfer reaction.[3] The reaction is favorable because of the high bond energy of the Si–O bond and the reaction is pushed to completion by the subsequent step to give a high yield of phosphine. We have examined[5] the corresponding reaction between sulfoxides and trichlorosilane and found that there is a dichotomy of behavior toward trichlorosilane between aromatic and aliphatic sulfoxides. Aromatic sulfoxides are reduced to the sulfides quantitatively whereas aliphatic sulfoxides are converted to the mercaptals and sulfides (reactions 2 and 3).

$$Ar_2S{=}O + HSiCl_3 \longrightarrow Ar_2S + HOSiCl_3 \qquad (2)$$

$$RCH_2{-}S{-}CH_2R + HSiCl_3 \longrightarrow$$
$$\underset{O}{\overset{\parallel}{}}$$

$$RCH(SCH_2R)_2 + RCH_2SCH_2R \qquad (3)$$

Amine oxides were found to be converted by chlorosilanes[4] to the corresponding amines (reaction 4).

Thus, deoxygenation by silane appears to be a general reaction and assumes increasing significance in the synthesis of phosphorus[6] and sulfur compounds.

There is still lacking however a mechanistic description of the intimate details involved in this type of oxygen-transfer reaction. We have undertaken therefore an investigation of the kinetics of reaction 2.

$$R_3N{\rightarrow}O + Cl_3SiSiCl_3 \longrightarrow R_3N + Cl_3SiOSiCl_3 \qquad (4)$$

Experimental Section

Materials. Diphenyl, di-*p*-chlorodiphenyl, and di-*p*-tolyl sulfoxide were commercially available (Aldrich) and were purified by recrystallization. Di-*p*-methoxydiphenyl sulfoxide was prepared by the method of Smiles and LeRossignol.[7] Trichlorosilane was obtained from Alfa Inorganics and was purified by distillation, bp 31.5° (760 mm), before use. Trichlorosilane-*d*, obtained from Merck Sharp and Dohme of Canada Ltd., was shown by nmr and mass spectrometry to be greater than 99% pure. Solvents used were purified by distillation from recommended drying agents.

Procedures. On a preparative scale the following procedure was used for reducing aromatic sulfoxides to the sulfides. To a solution of the sulfoxide (10 g) in dry ether (100 ml) in a three-necked flask fitted with a condenser protected by a drying tube (CaCl₂) and an addition funnel, a twofold excess of trichlorosilane in 50 ml of ether was added slowly. The solution was stirred for 1 hr. The excess silane was hydrolyzed with water and the ether was allowed to evaporate. The residue was taken up in boiling ethanol and filtered. The ethanol solution on cooling yielded the crystalline sulfide.

Kinetics. Using the fact that the ultraviolet spectra of sulfoxides and the corresponding sulfides are quite different (Table I), the kinetics of the reaction were studied photometrically. A Beckman DB spectrophotometer was used at constant wavelength to monitor the disappearance of sulfoxide or apearance of sulfide. The solutions of sulfoxides and silane used were equilibrated for a half-hour at the given temperature before each run. The temperature of the temperature-controlled cell holders was found to vary within ±0.1°.

Pseudo-first-order conditions were used for the reactions with an excess of (at least hundredfold stoichiometrically) silane. All runs were repeated at least once. The values of the pseudo-first-order rate constant (k') were calculated from plots of ln $(A_0 - A_\infty)/(A_0 - A_t)$ vs. time (t) by the method of least squares. The rate constants were calculated from the initial portion of the reaction for which first-order kinetics were seen to be valid, and for all com-

(1) For a review of some aspects of silicon hydride reactions in organic chemistry, see R. Calas, *Pure Appl. Chem.*, **11**, 61 (1966).

(2) H. Fritsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964); *ibid.*, **98**, 176 (1965).

(3) That reaction I is more of a deoxygenation was dramatically demonstrated by Mislow, *et al.*,[4] who found that phosphine oxide was converted to phosphine by perchloropolysilane Si_nCl_{2n+2}.

(4) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788, 7012 (1969).

(5) T. H. Chan, A. Melnyk, and D. N. Harpp, *Tetrahedron Lett.*, 201 (1969).

(6) See, for example, G. Maikl and R. Potthast, *ibid.*, 1755 (1968), for the synthesis of 1-phenylphosphol.

(7) S. Smiles and R. Le Rossignol, *Proc. Chem. Soc., London*, 745 (1908).

Table I. Physical Properties of Sulfoxides and Sulfides

Sulfoxide	Mp, °C	Cyclohexane λ_{max}, mμ	Log ϵ
Phenyl	70	226	(4.13)[a]
		267	(3.42)
p-Chlorophenyl	145	221	(4.18)[a]
		240	(4.29)
		286	(3.40)
p-Tolyl	91	237	(4.20)[a]
		275	(3.35)
p-Methoxyphenyl	98	229	(4.13)[b]
		251	(4.34)
		279	(3.69)

Sulfide	Bp or mp, °C		
Phenyl	295 (760 mm)	250	(4.08)[a]
	110 (20 mm)	274	(3.75)
p-Chlorophenyl	94	229	(4.18)[a]
		259	(4.19)
		286	(3.93)
p-Tolyl	55	252	(4.16)[a]
		276	(3.83)
p-Methoxyphenyl	42	234	(4.20)[b]
		256	(4.19)
		278	(3.94)

[a] Data from C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, and references quoted there. [b] Values obtained in this work.

Table II. Typical Run of the Reaction of p-Chlorophenyl Sulfoxide with Trichlorosilane in Cyclohexane[a]

Time, sec	Ln $(A_\infty - A_0)/(A_\infty - A_t)$
0	0
150	0.1248
300	0.2624
450	0.3901
600	0.5363
750	0.6580

[a] At 25°; [sulfoxide] = $\sim 10^{-4}$.

Figure 1. Typical plot of ln $(A_\infty - A_0)/(A_\infty - A_t)$ vs. time for the reaction of sulfoxide with trichlorosilane.

briefly consider them. Mechanism I involves the cleavage of the silicon hydrogen bond to yield a hydride. This is a possibility since, as we have already pointed out, the electronegativity of silicon is such that it would render the hydrogen hydridic. The sulfoxide would have to be involved either concomitant with the cleavage

Mechanism I

of Si–H bond as indicated or subsequent to the cleavage in a rate-determining step (rds).

Mechanism II is the opposite to that of I in that it involves a heterolytic fission of the Si–H bond into a silanion. An anion with negative charge residing on silicon has been proposed by Benkeser[8] to account for a number of amine-catalyzed reactions of trichlorosilane.

Table III. Rate Constants of the Reaction of Substituted Sulfoxide with Trichlorosilane[a]

Sulfoxide	k^1, sec^{-1}	[HSiCl$_3$] $\times$ 10^{-1} M	k, l. mol^{-1} sec^{-1}
p-Chlorophenyl	8.68 $\times$ 10^{-4}	2.210	3.93 $\pm$ 0.08 $\times$ 10^{-3}
	7.83 $\times$ 10^{-4}	1.940	4.40 $\pm$ 0.04 $\times$ 10^{-3}
Phenyl	1.95 $\times$ 10^{-3}	0.770	2.53 $\pm$ 0.05 $\times$ 10^{-2}
	1.92 $\times$ 10^{-3}	0.770	2.49 $\pm$ 0.01 $\times$ 10^{-2}
p-Tolyl	5.45 $\times$ 10^{-3}	0.469	1.16 $\pm$ 0.04 $\times$ 10^{-1}
	9.43 $\times$ 10^{-3}	0.810	1.16 $\pm$ 0.01 $\times$ 10^{-1}
p-Methoxyphenyl	1.06 $\times$ 10^{-2}	0.463	2.29 $\pm$ 0.04 $\times$ 10^{-1}
	2.07 $\times$ 10^{-2}	0.941	2.24 $\pm$ 0.01 $\times$ 10^{-1}

[a] In cyclohexane, at 25°.

pounds, first-order rates could be observed for at least two half-lives. Sample data are given in Table II and Figure 1.

Results and Discussion

Order of Reaction. The rate of reaction of phenyl sulfoxide with excess trichlorosilane in cyclohexane showed a first-order dependence on sulfoxide concentration. By varying the concentrations of trichlorosilane and using the expression

$$k = k'/[\text{HSiCl}_3]$$

a first-order dependence of rate on trichlorosilane concentration was also established (Table III).

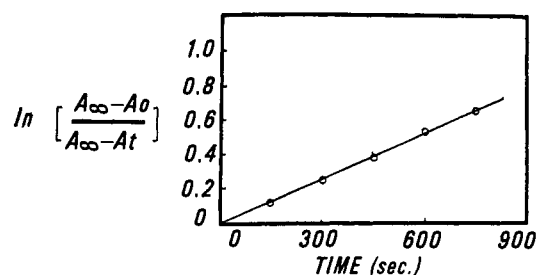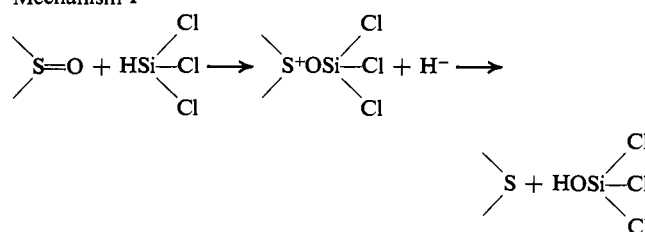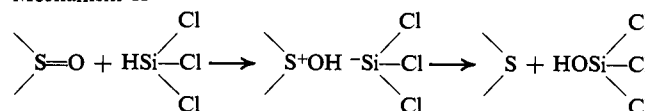Several reasonable mechanisms which are consistent with this kinetic result can be proposed. We can

Mechanism II

The inductive effect of chlorine may presumably be sufficient to overcome the electropositive nature of silicon to become negatively charged.

In mechanism III, the sulfoxide and the silane form a complex which then collapses into the products in some yet unspecified manner. There are ample examples in the literature to show that sulfoxides form complexes

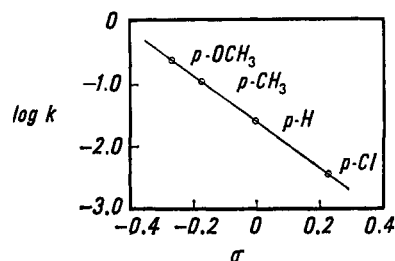(8) R. A. Benkeser, J. M. Gaul, and W. E. Smith, J. Amer. Chem. Soc., 91, 3666 (1969), and references cited therein.

Figure 2. Determination of the reaction constant, ρ, for the reaction of *para*-substituted phenyl sulfoxides with trichlorosilane at 25° in cyclohexane.

Figure 3. Arrhenius plot for the reaction of phenyl sulfoxide with trichlorosilane in cyclohexane.

with halosilanes. For example, silicon tetraiodide and tetrabromide complexes of diphenyl sulfoxide have

Mechanism III
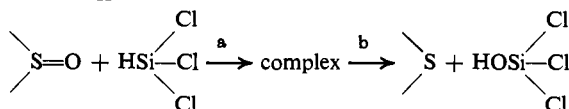
been isolated at low temperature.[9] At the present time, there is no need to specify whether a or b is the rds since both would give the second-order kinetics.

There are certainly other mechanisms which one can postulate; however, suffice it to say that mechanism III is vague enough to accommodate a spectrum of possibilities. It is imperative now to examine more experimental evidence before we have to delineate more clearly the details involved.

Substitution Effect. Various symmetrically substituted sulfoxides were reduced and the rate constants were plotted against Hammett's σ values (Table III and Figure 2). Since both phenyl rings are equally and equivalently substituted, the following expression can be used[10]

$$\log k/k_0 = n\sigma\rho$$

where n is the number of substituted rings. The negative ρ value obtained ($\rho = -1.54$) suggests that electron-withdrawing groups retard the reaction. This is to say that a nucleophilic mechanism is operative. This result suggests that in neither mechanisms I or II is the second step rate determining. It is difficult to predict at the moment the substituent effect for mechanism III. We will have to bear this point in mind when we expand on mechanism III later.

Solvent Effect. Chlorinated solvents[11] with increasing ionizing ability were selected to study the effect of solvent polarity[12] on rate of reaction (Table IV). Reactions reported to proceed through transition states with increased separation of charges have substantially larger increases in rate for solvent polarity increases paralleling ours. For example, Bartlett, *et al.*,[13] have reported that in the reaction of triphenylphosphine with elemental sulfur, in going from cyclohexane (ϵ 2.02) to benzene (ϵ 2.24), an eightyfold rate increase was observed.

(9) K. Issleib and A. Tzschach, *Z. Anorg. Allg. Chem.*, 305, 198 (1960).
(10) H. Jaffé, *Chem. Rev.*, 191 (1953).
(11) Consistent results could not be obtained from solvents such as tetrahydrofuran or dioxane.
(12) While dielectric constants may not be the best measure of solvent polarity on reaction rates, we could not find in the literature solvent parameters for either *n*-butyl chlorides or 1,2-dichloroethane.
(13) P. D. Bartlett and G. Maguerian, *J. Amer. Chem. Soc.*, 78, 3710 (1956).

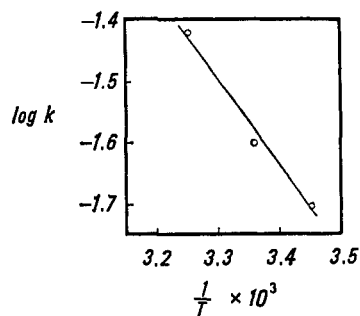While it is true that sulfoxide in its ground state possesses a considerable degree of polarization, the transition state involved in either mechanism I or II is expected to have even more charge separation. One would predict a substantial medium effect for either mechanism. The meager change in reaction rates observed in the present case would tend to eliminate either mechanism as the operative one.

Table IV. Rate Constants of the Reaction between Phenyl Sulfoxide and Trichlorosilane[a]

Solvent	Dielectric constant ϵ[b]	k, l. mol^{-1} sec^{-1}
Cyclohexane	2.02	$2.53 \pm 0.05 \times 10^{-2}$
		$2.49 \pm 0.01 \times 10^{-2}$
Carbon tetrachloride	2.23	$4.10 \pm 0.08 \times 10^{-2}$
		$4.69 \pm 0.18 \times 10^{-2}$
n-Butyl chloride	7.39	$1.67 \pm 0.02 \times 10^{-1}$
		$1.60 \pm 0.02 \times 10^{-1}$
1,2-Dichloroethane	10.0	$6.66 \pm 0.13 \times 10^{-1}$
		$6.88 \pm 0.07 \times 10^{-1}$

[a] In various solvents at 25°. [b] Values from NBS Circular 514, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards, 1951.

We must then scrutinize mechanism III more carefully. Issleib and Tzschach[9] reported the isolation of unstable coordination compounds of the formula $SiX_4(OS(C_6H_5)_2)$. Lappert and Smith,[14] in their ir investigation on the complexes of sulfoxides with group IV halides, suggested that the structure for the sulfoxide complexes can be represented by A in which oxygen is the donor atom. In the present case, we found that

$$R_2S{=}O \longrightarrow MX_n$$
$$A$$
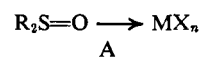
di-*p*-tolyl sulfoxide and trichlorosilane in absolute ether at $-78°$ gave a white precipitate. Under these conditions, only a trace of sulfide was detected. The precipitate can be isolated at $-78°$ and the solid decomposed at room temperature to give only di-*p*-tolyl sulfide. While we have not done any structural investigation of the complex, there is no reason to suggest that it is different from A. What is more important, the isolation of the complex precludes its formation being the rds in the mechanistic pathway.

Activation Parameters. Table V shows the rate constants obtained for the reaction of diphenyl sulfoxide in cyclohexane at various temperatures. The Arrhenius plot (Figure 3) yields $\Delta H = 7.1 \pm 0.5$ kcal/mol

(14) M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 3224 (1961).

Table V. Rate Constants of the Reaction between Phenyl Sulfoxide and Trichlorosilane[a]

Temp, °C	k, l. mol^{-1} sec^{-1}
17.8	$1.97 \pm 0.01 \times 10^{-2}$
25.0	$2.53 \pm 0.04 \times 10^{-2}$
	$2.49 \pm 0.01 \times 10^{-2}$
35.6	$3.88 \pm 0.04 \times 10^{-2}$
	$3.80 \pm 0.04 \times 10^{-2}$

[a] In cyclohexane at various temperatures.

Table VI. Rate Constants of the Reaction of Sulfoxide with Trichlorosilane-d[a]

Sulfoxide	k_H, l. mol^{-1} sec^{-1}	k_D, l. mol^{-1} sec^{-1}	k_H/k_D
Phenyl	2.52×10^{-2}	$1.09 \pm 0.05 \times 10^{-2}$ $1.02 \pm 0.04 \times 10^{-2}$	2.4 ± 0.1
p-Tolyl	1.16×10^{-1}	$0.62 \pm 0.02 \times 10^{-1}$ $0.57 \pm 0.01 \times 10^{-1}$	2.0 ± 0.1

[a] In cyclohexane at 25°.

and $\Delta S = -31 \pm 1.4$ eu.[15] The low value of enthalpy of activation reflects the facility and velocity of the reaction. The high decrease of entropy suggests the existence of a highly ordered transition state. In the collapse of complex A into the products, it must proceed through a transition state with severely restricted degree of randomness. We are tempted to suggest that a four-center transition state B is involved in the rds. A
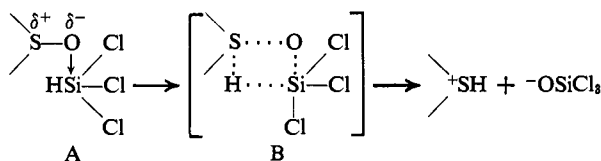
prominent feature of this transition state is that a pentacoordinate silicon and a "pentacoordinate" sulfur[16] are required. Sommer,[17] in his studies on the stereochemistry of silicon compounds, postulated a pentacoordinated silicon transition state for many displacement reactions. Aryl and perfluoroalkyl derivatives of sulfur tetrafluoride have been isolated and characterized[18] and "pentacoordinate" sulfur compounds have also been invoked as intermediate or transition state in organic reactions.[19] The transition state B must have considerable oxygen–silicon bond formation in order to account for the low enthalpy of activation. This would be in agreement with the substitution effect in which electron-donating groups were found to accelerate the reaction. There would also be slight increase in charge separation in the transition state and it accounts for the slight increase in the rate of reaction in more polar solvents.

Isotope Effect. To further elucidate the structure of the transition state we undertook to study the reaction of sulfoxide with trichlorosilane-d. The results are reported in Table VI. An isotope effect of $k_H/k_D = 2.0$–2.4 was observed.

The isotope effect for a silicon–hydrogen rupture in the rds has been calculated to be about 4 at 25°.[20–22] However, an experimental isotope effect of 1.15 for a Si–H rate-determining bond breakage has been reported by Kaplan and Wilzbach[20] for the reaction of tri-

organosilane with hydroxide. A value of 1.4 for the same reaction has been reported by Hammond, et al.[23] The explanation invoked for the apparantly low value of k_H/k_D is that considerable hydrogen bonding occurs in the transition state represented by C where HS is the solvent molecule. Recently, the primary isotope
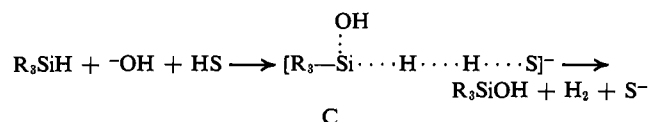
effect k_H/k_D of the carbonium ion silane hydride transfer reaction was found to be between 1.51 and 1.89.[24] The authors proposed a transition state for this reaction involving a four-center array such as D.
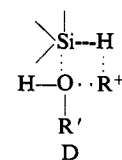
They argued that because of the triangular arrangement, the vibration of the Si–H bond which is lost resembles more of the Si–H bending mode, and since bending modes are of much lower frequency than stretching modes, the difference in zero-point energy will be much less and the observed isotope effect will be small. Our observed isotope effect of 2 can therefore be reconciled with the proposed four-center transition state B where simultaneous to the breakage of the Si–H bond, there is formation of a S–H bond.

Because of their obvious similarity, it is of interest to compare this reaction with the reaction between phosphine oxide and trichlorosilane. Horner and Balzer[25]

(15) Calculation of activation parameters was based on K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1963, p 378.

(16) The term "*pentacoordinate*" sulfur has been used to describe sulfur compounds of the type R_4S in which the electron pair is regarded as the "phantom" ligand; see ref 19.

(17) L. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw Hill Book Co., Inc., New York, N. Y., 1965.

(18) W. A. Sheppard, J. Amer. Chem. Soc., 84, 3058 (1962).

(19) B. M. Trost, R. LaRochelle, and R. C. Stkins, ibid., 91, 2175 (1969); see however, R. Tang and K. Mislow, ibid., 91, 5644 (1969).

(20) L. Kaplan and K. E. Wilzbach, ibid., 77, 1297 (1955).

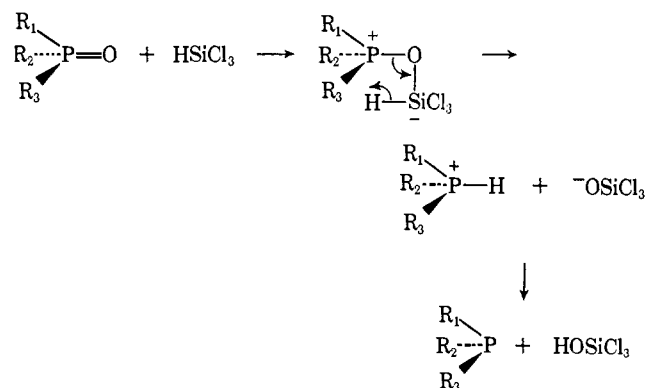(21) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press Co., New York, N. Y., 1960, Chapter IV.

(22) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 200.

(23) C. Brynko, G. E. Dunn, H. Gilman, and G. S. Hammond, J. Amer. Chem. Soc., 78, 4909 (1956).

(24) F. A. Carey and C-L. W. Hsu, J. Organometal. Chem., 19, 29 (1969).

(25) L. Horner and W. D. Balzer, Tetrahedron Lett., 1157 (1965).

observed that optically active phosphine oxide was reduced by trichlorosilane to give phosphine with retention of configuration. Based on this stereochemical observation, which is yet to be complemented by kinetics observation, the following mechanism was proposed.

Our kinetics results would then lend credence to this proposal. It should be pointed out that if an intermediate involving a phosphorane structure is proposed for this reaction, according to the stereochemical analysis of displacement reactions at phosphorus by

Mislow, et al.,[26] a cyclic constraint has to be introduced to account for the retention of configuration.

(26) K. E. Debruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969). See also P. D. Hensen, K. Naumann, and K. Mislow, *ibid.*, **91**, 5645 (1969).

π-Complexed β-Arylalkyl Derivatives. II. The Preparation and Acetolysis of 2-[π-(Aryl)chromium tricarbonyl]-2-methyl-1-propyl Methanesulfonates[1a]

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received October 27, 1969

Abstract: The π-(arene)chromium tricarbonyl complexes of 2-phenyl-2-methyl-1-propyl (neophyl) and p-methoxy-, p-methyl-, and m-methylneophyl methanesulfonates have been prepared and their acetolysis rates and products determined. At 75° the complexed derivatives are 1.8, 0.091, 0.45, and 0.91 times, respectively, as reactive as their noncomplexed counterparts. Each yields the π-aryl-migrated acetate, 3-[π-(aryl)chromium tricarbonyl]-2-methyl-2-propyl acetate, as the major product together with a mixture of π-complexed olefins. The acetolysis rates of the complexes at 75° are correlated by the relation log k (complex) $= -0.78\sigma^+ - 4.40$; those of the noncomplexed series by log $k = -2.35\sigma^+ - 4.56$. The meaning of these correlations is discussed and their difference is ascribed to a strong inductive electron withdrawal by the tricarbonylchromium combined with a conjugative effect which tends to suppress the ability of electron-donating aryl substituents to enhance the rate of acetolysis. Using the p-nitro group as a model for the inductive effect of the π-tricarbonylchromium it is estimated that the acetolysis rates of the complexed p-hydrogen-, p-methoxy-, p-methyl-, and m-methylneophyl methanesulfonates are enhanced by factors of 1600, 80, 400, and 800 times, respectively, at 75°. Steric buttressing, σ–π-type delocalization, and direct d-orbital bridging are considered as possible sources of the observed effect of π-complexation on the rates and course of these acetolyses.

In the previous paper of this series[2] we reported the acetolytic rates and products of chromium tricarbonyl-complexed D-, L-, DL-*threo*-, DL-*erythro*-3-phenyl-2-butyl, and DL-*erythro*-2-phenyl-3-pentyl methanesulfonates and compared them with those of the noncomplexed compounds. Among other effects we noted that prior π-complexation decreases the overall acetolysis rate slightly and inhibits aryl migration completely. After making a correction for the apparent inductive effect of the chromium tricarbonyl group we concluded that the acetolysis rates of the complexed *threo*- and *erythro*-3-phenyl-2-butyl methanesulfonates may be enhanced by factors of 33 and 6.8 times, respectively. Steric buttressing and inhibition of phenyl migration, σ–π-type delocalization, and direct d-orbital bridging were considered as possible sources of these effects but we were unable to make a clear distinction among them because so little was known about the electronic effect of the chromium tricarbonyl

group itself. In order to examine this aspect of the problem in greater detail and to ascertain whether a π-complexed aryl group would migrate under more favorable circumstances, we have prepared and examined the acetolytic reactivities of a series of chromium tricarbonyl-complexed 2-phenyl-2-methyl-1-propyl- (neophyl-) type methanesulfonates.

Methods and Results

Each of the required methanesulfonates, 1- to 4-OMs, was prepared from the known 2-aryl-2-methyl-1-propanol[3] in the usual manner[2] and converted to the yellow, crystalline, apparently air stable, chromium tricarbonyl complex as described previously,[2] cf. Chart I.

Acetolyses of these primary methanesulfonates were conducted and the products were determined in the manner described earlier.[2] Control experiments were again employed to demonstrate that the decomplexation and reduction procedure used in the analysis of the complexed derivatives did not isomerize the organic

(1) (a) Portions of this work were presented at the 38th Annual Meeting of the South Carolina Academy of Science, Columbia, S. C., April 1965 [*Bull. S. Carolina Acad. Sci.*, **XXVII**, 52 (1965)] and at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstract 008S; (b) NSF Trainee 1968–1970.
(2) R. S. Bly and R. L. Veazey, *J. Amer. Chem. Soc.*, **91**, 4221 (1969).

(3) (a) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *ibid.*, **65**, 1469 (1943); (b) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (c) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).